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(19)

(54) METHOD FOR CONTROLLING AN AQUEOUS COATING BATH CONTAINING A WATER-SOLUBLE OR DISPERSIBLE COATING COMPOSITION

(71) We, MITSUBISHI RAYON CO. LTD., a corporation organized under the laws of Japan, of 8, Kyobashi-2-chome, Chuo-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method for controlling an aqueous coating bath in which there is used as a replenishing paint for the bath a paint binder which has been subjected to anion exchange treatment followed by cation exchange treatment.

Many aqueous coating compositions containing, as the main component, a water-soluble or dispersible polycarboxylic acid resin, have been known and used widely in the field of coating compositions for dipping or electrodeposition. Recently, the progress of polymerization technique has resulted in the development of polycarboxylic acid resins suitable for one-coat finish by an electrodeposition coating method. Since the dispersion stability of the polycarboxylic acid resin in an aqueous medium is not sufficient, a neutralizing agent for the polycarboxylic acid resin has to be present in the bath. This neutralizing agent accumulates in the aqueous coating bath containing the resin as the coating proceeds resulting in variations in the coating film formed on a substrate by coating it in said coating bath, so that the film tends to be inferior in for example gloss, corrosion-resistance, and weather-resistance.

Various methods have been proposed for removing this disadvantage. For example, Dutch Patent Application No. 6,815,277 discloses an improvement in the characteristics of the polycarboxylic acid resin used. British Patent No. 972,169 discloses using, as a replenishing paint, a polycarboxylic acid resin having a lower degree of neutralization than that of the polycarboxylic acid resin salt used for preparing the coating bath in order to neutralize the excessive neutralizing agent accumulated in the coating bath. French Patent No. 1,431,389 teaches providing anodes separated by a diaphragm in a coating bath and taking the amine gathered in the neighbourhood of the anodes out of the bath, thereby preventing the excessive neutralizing agent amine from being accumulated in the coating bath. Further, French Patent No. 1,439,867 and British Patent No. 1,030,204 disclose providing an electrical dialyzer in a coating bath, by which the excessive amine accumulated in the coating bath is taken out of the bath, and British Patent No. 1,033,833 discloses treating a coating bath with a cation exchange resin to remove the excess of amine present in the bath. Moreover, in the Paint Oil and Colour Journal, August 14, 1970, page 24, it is described that the coating bath is filtered through a membrane filter to discharge the excessive amine from the bath.

These methods, however, require continuous measurement of the amount of neutralizing agent present in the coating bath, and hence, require complicated operations. In addition, these methods require apparatus for removing accumulated neutralizing agent from the bath, and hence, are disadvantageous from the economic point of view. Furthermore, the amount of neutralizing agent present in the coating bath is always varied, whereby the solubility of the polycarboxylic acid resin in the coating bath is also varied, and therefore, the characteristics of the coating film formed on a substrate by coating it with such a coating bath, particularly the gloss, corrosion-resistance and weather-resistance of the coating, are varied, and uniform coating films cannot continuously be obtained. Such a phenomenon becomes a very great bar to the one-coat finish method. At least the following two conditions are required to be satisfied for obtaining an aqueous coating composition having no disadvantages mentioned above and obtaining coating films having excellent characteristics from this coating composition: The first is that the coating bath containing the polycarboxylic acid resin salt does not cause any change with the lapse of time, and the second is that the paint particles consisting essentially of a polycarboxylic acid resin contained in the aqueous coating bath do not cause any change with the lapse of time.

The present inventors have found that when coating is effected while replenishing a coating bath with a fresh coating composition corresponding to the amount of the coating composition taken out of the bath as the coating proceeds to maintain the amount of the nonvolatile matter present in the bath at M_o, the amount of the neutralizing agent present in the bath, A, and the amount of the neutralizing agent per the unit amount of the nonvolatile matter in the bath, C_b, can be shown by the following equations:

$$A=M_o(C_a-C_o)T+A_o \qquad [C]$$

$$C_b=(C_a-C_o)T+C_b^{\circ} \qquad [D]$$

wherein A refers to the amount of the neutralizing agent present in the aqueous coating bath containing a polycarboxylic acid resin salt at any time, A_o to the amount of the neutralizing agent in the coating bath just before the beginning of coating, M_o to the amount of the non-volatile matter present in the coating bath at the beginning of coating, C_a to the amount of the neutralizing agent per the unit amount of the non-volatile matter in the replenishing coating composition, C_o to the amount of the neutralizing agent per the unit amount of the nonvolatile matter in the coating composition taken out of the bath by coating, T to m/M_o in which m is the amount of the nonvolatile matter taken out of the bath by coating, the time at which m becomes M_o being called one turnover, C_b to the amount of the neutralizing agent per the unit amount of the nonvolatile matter in the bath at any time, and C_b° to the amount of the neutralizing agent per the unit amount of the nonvolatile matter present in the coating bath just before the beginning of coating.

In the conventional coating method, an aqueous coating bath containing a polycarboxylic acid resin salt is used, and as coating proceeds, the bath is replenished with a coating composition containing a polycarboxylic acid resin salt corresponding to the amount of the non-volatile matter taken out of the system. However, in the prior art method, the amount of the neutralizing agent per the unit amount of the nonvolatile matter in the coating composition taken out of the bath by coating is always smaller than that of the neutralizing agent per the unit amount of the nonvolatile matter in the coating composition present in the bath. That is, $C_b^{\circ}>C_o$. When such a phenomenon is caused, the solubility in water of the coating composition present in the bath is varied, and it is difficult to continuously form a standardized coating film by effecting coating in such a coating bath. In order to avoid this disadvantage, methods as in British Patent Nos. 972,169 and 1,030,204 and French Patent No. 1,439,867 have been proposed. These methods, however, are economically disadvantageous, because they require a complicated operation for always checking the amount of the neutralizing agent present in the bath or require an expensive apparatus.

According to the invention, we provide a process for controlling an aqueous coating bath containing a water-soluble or dispersible paint binder, which comprises:

(a) copolymerizing (1) 5 to 80 mole percent of at least one compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-COOR_1 \qquad (E)$$

wherein R is H or CH_3 and R_1 is a straight or branched alkyl group having 1 to 18 carbon atoms or benzyl, (2) from 0.1 to 60 mole percent of a compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-CONHR_3 \qquad (F)$$

wherein R is the same as defined above, R_3 is H or a $-CHR_4OR_5$ group in which R_4 is hydrogen or an alkyl group having 1 to 8 carbon atoms and R_5 is a straight, branched or cyclic alkyl group having 1 to 8 carbon atoms and/or a compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-COOR_6OH \qquad (G)$$

wherein R is the same as defined above, and R_6 is a substituted or unsubstituted alkylene having 1 to 8 carbon atoms, (3) 1 to 30 mole percent of (H) an α,β-monoethylenically unsaturated carboxylic acid or its anhydride and (4) 5 to 40 mole percent of (I) at least one other vinyl monomer copolymerizable with the monomers (E) to (H), the total sum of components (E) to (I) being 100 mole percent, to prepare a paint binder, the paint binder being composed mainly of a partial neutralization salt of a polycarboxylic acid resin having a pKa(r) and an n value defined by the equation [A] and low molecular weight acids or their salts having a pKa(e) value defined by the equation [B], the main polycarboxylic acid resin having, when the paint binder is diluted with water, an average pKa(r) value defined by the formula [A] of 8.0 or more and having an n value of $0.8 \leqq n \leqq 2.5$,

$$pH=pKa(r)+n\log\frac{\alpha}{1-\alpha} \qquad [A]$$

wherein pKa(r) is a constant represented by $-\log Ka(r)$ in which Ka(r) is the dissociation constant of the acid groups of the polycarboxylic acid resin in water; α is the degree of neutralization of the whole of the acid groups of the polycarboxylic resin with a neutralizing agent and has a value within the range defined by $0.15 \leqq \alpha \leqq 0.80$; and n is a constant obtained experimentally by use of the equation [A] and has a value within the range defined by $0.8 \leqq n \leqq 2.5$; the pKa(e) value defined by equation [B] when the low molecular weight acids or their salts in the paint binder are diluted with water being at least 0.5 smaller than the pKa(r) value of the main polycarboxylic acid resin constituting the paint binder

$$pH=pKa(e)+\log\frac{\alpha}{1-\alpha} \qquad [B]$$

wherein pKa(e) is a constant represented by $-\log Ka(e)$ in which Ka(e) is the dissociation constant of the low molecular weight acids or their salts in water; and α is the degree of neutralization of the whole of the acid groups of the low molecular weight acids with a neutralizing agent; (b) adding an anion exchanger to the paint binder or its partial neutralization product alone or in admixture with a pigment and, if necessary, a small amount of water with stirring to react the low molecular weight acids or their salts with the anion exchanger and then removing the anion exchanger from the paint binder to make the content of the low molecular weight acids or their salts in the paint binder up to 5%,

(c) adding up to 60% by weight of deionized water or water which constitutes a coating bath, or water obtained by removing the paint particles from a coating bath to the paint binder obtained in above (b) and then contacting the paint binder with a cation exchanger, thereby reacting the cation exchanger with the excess neutralizing agent contained in the paint binder and then removing the cation exchanger from the paint binder,

(d) diluting the paint binder obtained in above (c) with deionized water to a given concentration to prepare an aqueous coating bath, and

(e) supplying to the aqueous coating bath the paint binder obtained in above step (c) to control the paint concentration of the aqueous coating bath to a given value in order to prevent the reduction of the paint concentration of the aqueous coating bath due to the paint being taken out of the coating bath with the progress of coating in the aqueous coating bath obtained in above (d).

When a water-soluble or dispersible coating composition is prepared by use of the paint binder composed of a polycarboxylic acid resin salt and then dissolved or dispersed in water to form an aqueous coating bath, the characteristics of the said resin in this coating bath are defined by the equation [A]. The polycarboxylic acid resin used in the present invention is usually a mixture of polymers having different pKa values (i.e., the polycarboxylic acid resin has a considerably wide distribution of degree of polymerization and composition). Therefore, when said polycarboxylic acid resin is dissolved or dispersed in water, a uniform aqueous bath is temporarily formed. However, with the lapse of time, the polycarboxylic acid resin is precipitated from the bath. This is because materials having a pKa value smaller than that of the main polymer constituting the polycarboxylic acid resin, particularly at least 0.5 smaller than the pKa(r) value of the latter, said materials being mainly low molecular weight polymers having a high carboxylic acid content and unpolymerized materials included in the polycarboxylic acid resin, are more water-soluble than the main polycarboxylic acid polymer, and hence, the materials are dissolved into water from the coating composition particles in the aqueous bath to vary the dispersion equilibrium of the aqueous bath. In order to prepare resins which do not exhibit such disadvantages, the polycarboxylic acid resin is treated with an anion exchanger to make 5% or less the content of the impurities having a lower pKa value contained in the resin. Further, a small amount of water and/or a vinyl monomer copolymerizable with the remaining unsaturated carboxylic acid may be added to

the polymerization system at the end of polymerization of the vinylic polycarboxylic acid, the polymerization completed and the thus obtained polycarboxylic acid polymer then treated with an anion exchanger.

The α,β - monoethylenically unsaturated carboxylic acid or its anhydride (H) may be a monomer having the formula (Z) and/or its half alkyl ester, in which m is 1 or 2:

$$CH_2=\underset{|}{C}-COOH \qquad (Z)$$
$$(CH_2)_m COOH.$$

In this case, the (2) component may consist of 5 to 40 mole percent of the formula (F) monomer and 5 to 40 mole per cent of the formula (G) monomer, the total sum of the two being 10 to 60 mole percent.

In step (b), 15% by weight or less of water may be added to the salt of the polycarboxylic acid resin or its salt and the resulting mixture treated with an —OH type anion exchange resin.

The polycarboxylic acid resin may be in the form of a mixture with an epoxy resin and/or a melamine resin in a ratio of 100/0 to 60/40.

The vinyl monomers represented by the formula [E] are acrylates or methacrylates in which R_1 is an alkyl, for example, methyl, ethyl, n-propyl, iso-propyl, sec-butyl, t-butyl, pentyl, 2-ethylhexyl, nonyl dodecyl, or stearyl; or benzyl.

The vinyl monomers represented by the formula [F] are acrylamides or methacrylamides in which R_3 is H or $-CHR_4OR_5$. The groups represented by OR_5 include methoxy, ethoxy, n-propoxy, n-butoxy, pentoxy or cyclohexoxy, and the alkylene groups represented by $-CHR_4-$ include methylene and alkylmethylene.

The vinyl monomers represented by the formula [G] are monoesters of diols with acrylic or methacrylic acid, and as said diols, there may be used ethylene glycol, propylene glycol, 1,3-butylene glycol, 1,4-butane diol, hexylene glycol, 2-ethylhexylene glycol and the like.

The α,β-monoethylenically unsaturated carboxylic acid may be acrylic acid, methacrylic acid, itaconic acid, α-methylene glutaric acid, itaconic acid half ester and α-methylene glutaric acid half ester in which the half ester is selected from methyl ester, ethyl ester, butyl ester, propyl ester, hexyl ester, octyl ester and the like. The copolymerizable vinyl monomers (I) may be any vinyl monomer provided that it is copolymerizable with the monomers (E) to (H). Examples of such monomers (I) are styrene, α-methylstyrene, vinyl chloride, vinyl acetate, vinyl propionate, vinyl esters of Versatic Acid, acrylonitrile and methacrylonitrile.

Among these monomers, the component (E) is required to be copolymerized in a proportion of 5 to 80 mole percent, and if it is present in a proportion of less than 5 mole percent in the copolymer, the coating film resulting from the copolymer is inferior in characteristics, particularly gloss, weather-resistance. On the other hand, if the component (E) is present in a proportion of more than 80 mole percent in the copolymer, the coating film resulting therefrom tends to have a decreased hardness, stain resistance, impact resistance and the like. Therefore, such copolymers are not desirable

The α,β-monoethylenically unsaturated carboxylic acid (H) is required to make the resulting copolymer water-soluble or water-dispersible by neutralization. When this component is copolymerized in a proportion of less than 1 mole percent, the resulting copolymer is inferior in affinity to water and hence cannot be used for the purpose of the present invention. On the other hand, when said component is copolymerized in a proportion of more than 30 mole percent, the affinity of the resulting copolymer to water becomes good, but the water-resistance and corrosion-resistance of the coating film formed from such copolymer are degraded. Therefore, the use of more than 30 mole percent of the carboxylic acid (H) is not practicable. Thus, itaconic acid and α-methylene glutaric acid which are relatively hydrophobic and have excellent copolymerizability to obtain a sharp distribution of polymer composition among these acids show excellent effects in the present invention, particularly in the preparation of an aqueous coating composition having a one-coat finish adaptability.

The components represented by the formulas (F) and (G) are for imparting heat-cross-linkability to the vinyl polymer, and are present in the copolymer in a total proportion of from 0.1 to 60 mole percent, particularly 10 to 60 mole percent.

A film formed from the thus obtained copolymer is heated to be cross-linked, whereby the resulting film becomes excellent in gloss, weather-resistance, hardness and corrosion-resistance. In order to make good the properties of a film formed from an aqueous coating composition having a one-coat finish adaptability, it is necessary that the polycarboxylic acid resin which is the main constituent of the coating composition is as hydrophobic as possible. For satisfying this condition, the characteristic value pKa(r) which indicates the acidity of the polycarboxylic acid resin must be 8.0 or more and the degree of neutralization of the polycarboxylic acid resin with a base must be within the range of $0.15 \leqq \alpha \leqq 0.80$. A polycarboxylic acid resin having a pKa(r) value of less than 8.0 has too low a thermal flowability to form a film hav-

ing excellent gloss. Further, this resin is hydrophilic, and hence, a film formed from this resin has low resistance to water, corrosion and alkali. When the α value of the polycarboxylic acid resin is less than 0.15, it becomes impossible to dissolve or disperse the resin in water. On the other hand, when the α value is more than 0.80, the water-solubility of the resin is too high and the thermal flowability of the resin is too low, whereby the water resistance and corrosion resistance of a film formed from the resin is lowered.

In this invention, the paint binder composed mainly of the polycarboxylic acid resin preferably doesn't contain an emulsifying agent. As the paint binder containing an emulsifying agent is hydrophilic, the coating films formed from the said paint binder have low water resistance, whether resistance, and resistance to alkali and corrosion.

When an aqueous coating bath is prepared from a polycarboxylic acid resin containing materials having a pKa value smaller than the pKa(r) value of the main constituent of the polycarboxylic acid resin, said materials migrate into water because they are more water-soluble than the polycarboxylic acid resin. Therefore, an aqueous coating bath formed from such a polycarboxylic acid resin liberates materials having a lower pKa value into water with the lapse of time to break the equilibrium of the aqueous coating bath, whereby paint particles consisting mainly of the polycarboxylic acid resin are precipitated. Such a disadvantage appears remarkably where the polycarboxylic acid resin contains more than 5% of materials having a pKa value at least 0.5 smaller than the pKa(r) value of the main constituent of the polycarboxylic acid resin.

In the present invention, therefore, it is necessary that the amount of the lower pKa materials contained in the polycarboxylic acid resin is 5 % or less, preferably 1 % or less. Almost all of the lower pKa materials contained in the polycarboxylic acid resin used in the present invention are low molecular weight polymers containing carboxylic acid groups remaining incompletely polymerized or unpolymerized unsaturated acids. The method for rendering the content of such lower pKa materials small comprises treating the polycarboxylic acid resin or its salt with an anion exchanger. According to this method, the content of the lower pKa materials in the resin can be 5 % or less. The treatment with an anion exchanger in this method includes treatments with zeolite, alumina, silica, activated carbon, diatomaceous earth, an ion exchange resin, an ion exchange membrane and the like and the application of a dialysis or electrical dialysis, and the treatment with an anion exchange resin, particularly having a particle size of 1,200 microns or less, can exhibit the most excellent effect. When the particle size is more than 1,200 microns, the ability to treat the polycarboxylic acid resin is lowered. As the salt type of anion exchange resin, there may be used SO_4^{-} Cl^{-}, OH^{-}, NO_3^{-} or other various salt types, though the OH^{-} type can exhibit the most excellent effect.

The treatment of the polycarboxylic acid resin or its salt with the anion exchanger may be achieved by mixing the resin with an anion exchanger having a particle size of 1,200 microns or less with stirring, if necessary, with water. The most effective method comprises mixing the polycarboxylic acid resin, pigments, the anion exchange resin and, if necessary, water and then grinding the resulting mixture. By use of this method, the content of the lower pKa materials in the polycarboxylic acid resin can be rendered 1 % or less. The treatment with an anion exchanger is preferably applied to a polycarboxylic acid resin neutralised with an amine or ammonium. According to this method, the lower pKa materials contained in the polycarboxylic acid resin can be easily dissociated.

An optional additional treatment for rendering the content of the lower pKa materials small comprises adding water and/or a vinyl monomer towards the end of the polymerization process for producing the vinylic polycarboxylic acid resin and completing the polymerization. According to this method, the polymerizability of the vinylic polycarboxylic acid can be enhanced, whereby the content of a low molecular weight polymer of the acid having a lower pKa value or unpolymerized acid can be rendered very small. The thus obtained polycarboxylic acid resin is then treated with an anion exchanger according to the method described above.

After neutralising the polycarboxylic acid resin obtained by the above-mentoined method with a base, the neutralized resin is diluted with deionized water to form an aqueous coating bath. When coating is effected in the thus obtained bath, the bath is replenished with a fresh coating composition corresponding to the nonvolatile matter taken out of the bath by coating. In this case, the prior art method replenishes the bath with a coating composition having a relation of $C_a > C_m$, and hence, an excess of a neutralizing agent is accumulated in the bath with the progress of coating. Therefore, the dispersion state of paint particles iln the bath is varied with the lapse of time, and hence, a film formed from such a bath does not meet the desired standard and the characteristic properties thereof is deteriorated.

In order to remove said disadvantage, the coating composition with which the bath is replenished must have a degree of neutralization of $C_a = C_m$. Further, in the preparation of an aqueous coating bath, a coating composition having $C_a = C_m$ is preferably used,

whereby the amount of the neutralizing agent in the bath can always be maintained constant and the control of the coating bath becomes very easy.

In order to satisfy such conditions, it is necessary to add 60 % or less of water to a paint binder consisting essentially of a polycarboxylic acid resin or its salt having a lower pKa impurity content of 5 % or less, preferably 1 % or less and then treat the resulting mixture with a cation exchanger. The thus obtained paint binder contains the minimum amount of the neutralizing agent necessary for the resin component to be stably dispersed in water, and hence, can satisfy the relation of $C_a \doteqdot C_e$. When such a paint binder is used in the preparation of an aqueous coating bath and as a replenishing paint, the neutralizing agent is substantially not accumulated in the bath with the progress of coating.

In the present invention, the amount of water added to the paint binder consisting essentially of a polycarboxylic acid resin or its salt is 60 % by weight or less, preferably 15 to 60 % by weight. When the water added is too little, the effect of the present invention cannot sufficiently be achieved. Further, when 60 % by weight of water is added, it follows that a considerably large amount of a neutralizing agent is removed from the polycarboxylic acid resin salt, and hence, the dispersion stability of the paint binder in water is lower in some cases.

The polycarboxylic acid resin or its salt used in the present invention is required to have a lower pKa impurity content of 5 % or less, preferably 1 % or less. When a polycarboxylic acid resin or its salt containing more than 5 % of said impurities is treated with a cation exchanger according to the present process, no effect aimed at by the present invention can be accomplished. The cation exchangers which may be used in the present invention are ion exchange resins and the like. Cation exchange type ion exchange resins exhibit the most excellent effect. As the cation exchange resin, there may be used various salt types, such as H type, Na type, K type and the like, though the use of H type cation exchange resins results in the most excellent effect.

The coating in an aqueous coating bath prepared by use of a paint binder containing the polycarboxylic acid resin or its salt obtained in a manner as mentioned above is effected as follows:

The paint binder treated with a cation exchanger is diluted with deionized water to a solids concentration of 1 to 20 % by weight to form an aqueous coating bath. Since some of the coating composition is taken out of the bath by coating, the bath is replenished with a coating composition prepared by suitably diluting the paint binder treated with a cation exchanger with deionized water or the above aqueous coating bath.

Using the above-mentioned method, substantially no accumulation of an excess of neutralizing agent is caused in the aqueous coating bath, and hence, the control of the coating bath is very easy as compared with the prior art method. Further, a film formed from the coating bath has excellent properties.

In the present invention, the polycarboxylic acid resin may be colored by inorganic or organic pigments, for example, titanium oxide, carbon black, cobalt blue, ultramarine blue, ceruleum, manganese chromium green, yellow iron oxide, cadmium yellow, phthalocyanine blue and the like. Strontium chromate and the like may be used as anticorrosive pigment.

In order to enhance the properties of a film obtained from the present aqueous coating composition, epoxy resins, aminoplasts and other plasticizers may be added to the composition. As the aminoplasts, N-alkoxymethylmelamines are preferable and N-alkoxymethylmelamines having 1 to 4 carbon atoms in the alkyl group are particularly preferable. Further, as the epoxy resins, there are preferable those having an epoxy equivalent of 100 to 2,000 and particularly preferable is a reaction product of bisphenol A with epichlorohydrin. As the other plasticizers, octyl phthalate, nonylphenyl phthalate and butyl Cellosolve (Registered Trade Mark for ethylene glycol monoethyl ether) may be illustrated.

The water-dispersible or soluble coating composition obtained by the method of the present invention has a good dispersion stability in water, and when coating proceeds, substantially no accumulation of an excess of neutralizing agent in the bath is caused. Therefore, the control of the coating bath is very easy. Since the water-soluble or dispersible coating composition of the present invention is relatively hydrophobic, a film formed from this coating composition has excellent gloss and corrosion-resistance. Accordingly, a film formed by one-coat finish according to an electrodeposition coating using said water-soluble or dispersible coating composition is not inferior in any respect to a film formed from a conventional solvent-type paint. In addition, even when a substrate having a portion at which plates are piled on each other is coated with the present coating composition, substantially no paint flows out from the slit of the piled portion.

The invention is further explained below referring to Examples which are only by way of illustration and not by way of limitation.

Comparative Example.

Into a flask equipped with a stirrer, a reflux condenser and a thermometer were charged the following components, the temperature was elevated to 70°C over 2.5 hrs., at which tem-

perature the polymerization was effected for 5.5 hours, after which the temperature was further elevated to 75°C, at which temperature the reaction mixture was maintained for 4 hours.:

2-Ethylhexyl acrylate	39.9	parts by weight
Styrene	25.8	,, ,, ,,
n-butoxymethyl acrylamide	19.1	,, ,, ,,
Itaconic acid	3.23	,, ,, ,,
Azobisisobutyronitrile	2.93	,, ,, ,,
2-Mercaptoethanol	1.12	,, ,, ,,
Isopropyl alcohol	62.5	,, ,, ,,

The thus obtained resin solution is designated as 1a.

In the same manner as above, the following components were subjected to polymerization to obtain a resin solution 1b:

Ethyl acrylate	24.8	parts by weight
Styrene	22.8	,, ,, ,,
n-butoxymethyl acrylamide	19.1	,, ,, ,,
Itaconic acid	3.23	,, ,, ,,
Azobisisobutyronitrile	2.93	,, ,, ,,
2-Mercaptoethanol	1.12	,, ,, ,,
Isopropyl alcohol	4.74	,, ,, ,,

In the same manner as above, the following components were subjected to polymerization to obtain a resin solutoin 1c:

2-Ethylhexyl acrylate	39.9	parts by weight
Styrene	25.8	,, ,, ,,
n-butoxymethyl acrylamide	18.4	,, ,, ,,
Itaconic acid	3.0	,, ,, ,,
Acrylamide	1.0	,, ,, ,,
Azobisisobutyronitrile	2.93	,, ,, ,,
2-Mercaptoethanol	1.12	,, ,, ,,
Isopropyl alcohol	62.5	,, ,, ,,

In the same manner as above, the following components were subjected to polymerization to obtain a resin solution 1d:

Butyl acrylate	33.3	parts by weight
Styrene	27.1	,, ,, ,,
Acrylic acid	1.0	,, ,, ,,
n-butoxymethyl acrylamide	22.0	,, ,, ,,
Itaconic acid	3.63	,, ,, ,,
Isopropyl alcohol	66.6	,, ,, ,,
Azobisisobutyronitrile	3.37	,, ,, ,,
2-Mercaptoethanol	1.26	,, ,, ,,

In the same manner as above, the following components were subjected to polymerization to obtain a resin solution 1e:

Ethyl acrylate	26.3	parts by weight
Methyl methacrylate	10.8	,, ,, ,,
Styrene	5.0	,, ,, ,,
n-butoxymethyl acrylamide	9.8	,, ,, ,,
Itaconic acid	0.98	,, ,, ,,
2-Mercaptoethanol	0.188	,, ,, ,,
Azobisisobutyronitrile	2.2	,, ,, ,,
Isopropyl alcohol	43.6	,, ,, ,,

The resin solutions 1a—1e were neutralized with β-dimethylaminoethanol to an apparent neutralization degree α of 0.30 to 0.80 to form several neutralized solutions having different neutralization degrees for each resin solution. The thus neutralized solutions were diluted with deionized water to a solids concentration of 10 % to form aqueous coating baths. The pH values of the resulting baths were measured at 25°C. From the relation between the pH values thus obtained and log $\frac{\alpha}{1-\alpha}$ in which α is the degree of neutralization of the polycarboxylic acid resin with a neutralizing agent (i.e., the equivalent ratio of β-dimethylaminoethanol to the apparent COOH groups in the resin), the pKa(r) values and the n values were calculated according to the equation [A]. The results obtained were as shown in Table 1.

Table 1

Kind of resin	1a	1b	1c	1d	1e
pKa(r)	8.8	7.8	9.12	9.12	8.23
n	1.15	1.20	0.98	0.96	1.09

The resin solutions 1a, 1b, 1c, 1d and 1e were neutralized with β-dimethylaminoethanol to an apparent neutralization degree α of 0.45 to obtain neutralized resin solutions 1a′, 1b′, 1c′, 1d′ and 1e′, respectively, which were then mixed in a proportion as shown in Table 2. The thus obtained mixed resin solutions were formed into paints by the following procedure: 75 parts by weight of titanium oxide JR—600E (trade name of Teikoku Kako Co., Ltd.) was added to 100 parts by weight of the mixed resin solution, the resulting mixture

was mixed on a ball mill for 24 hours and then 200 parts by weight of the mixed resin solution was added thereto, after which mixing was continued for a further 24 hrs. to obtain a white enamel paste. The white enamel paste obtained was diluted with deionized water to a solids content of 10 % by weight to prepare an aqueous coating bath.

A zinc phosphate-treated iron plate (Bondelite #100) was coated under the following conditions: Voltage: 80 V; temperature: 25°C; electrodeposition time. 3 min. The thus obtained coated plate was baked at 180°C for 30 min. The stability of the bath and the gloss value of a film obtained were as shown in Table 2.

Table 2

Resin blend system	No.	Resin weight fraction ratio	Stability of coating bath	Gloss value 60^o - 60^o of film obtained (%)		Difference of pKa(r) (absolute)
				1st day from preparation of bath	7th day from preparation of bath	
1a'/1b'	1	1/0(1a)	Good	87.8	94.5	0.
	2	8/2	Bad	61.8	4.9	1.0
	3	5/5	Bad	23.4	29.0	1.0
	4	2/8	Somewhat bad	55.1	51.5	1.0
	5	0/1	Good	61.5	41.6	0
1a'/1e'	6	1/0(1a)	Good	89.0	-	0
	7	8/2	Somewhat bad	75.2	-	0.57
	8	5/5	Bad	37.9	-	0.57
	9	2/8	Bad	48.0	-	0.57
	10	0/1	Good	79.0	-	0

TABLE 2 (Continued)

Resin blend system	No.	Resin weight fraction ratio	Stability of coating bath	Gloss value 60° - 60° of film obtained (%)		Difference of pKa(r) (absolute)
				1st day from preparation of bath	7th day from preparation of bath	
	11	0/1(1d)	Good	76.6	75.0	0
	12	2/8	Good	73.7	77.0	0
1c'/1d'	13	5/5	Good	83.5	77.7	0
	14	8/2	Good	82.3	75.1	0
	15	1/0	Good	76.0	73.2	0

As is clear from Table 2, the stability of the coating baths (Nos. 2, 3, 4, 7, 8 and 9) obtained by use of the mixed resins in which a resin having a difference in pKa(r) from the main resin constituting the coating composition of at least 0.5 is mixed is bad. Further, the gloss value of film formed by electrodeposition coating is also low. On the other hand, the stability of the coating baths Nos. 1, 5, 6, 10, 11, 12, 13, 14 and 15 is good, and the gloss value of the film formed by electrodeposition coating is high. In the above table, gloss value was measured according to 60°—60° mirror surface reflection method (hereinafter the gloss value is measured by this method).

The white enamel obtained from the resin solution of 1c′ as the same method as above was diluted with deionized water to a solids content of 13 % by weight to prepare a coating bath. After the preparation of the coating bath, electrodeposition was effected every day at 80V at 25°C for an electrodeposition time of 2.5 min., and the gloss value of the film obtained and the specific conductivity of the bath were measured to obtain results as shown in Table 3.

Table 3

Days	Solids conc. (%) N.V.	Specific conductivity per 1% of solids (K/C(10^2 $\mu \mho$ /cm))	Gloss (%)
0	12.9	0.170	86
2	12.8	0.218	80
4	12.7	0.248	76
6	12.7	0.283	72
8	12.4	0.320	70
10	12.3	0.341	70

The cause of an increase of specific conductivity of the coating bath was found to be the amine salt of unpolymerized itaconic acid contained in the paint particles in the bath by the analysis of the behaviour of pH in the aqueous coating bath, the measurement of the double bond content in the water in the bath, the measurement of infrared absorption spectrum, the variation of the amount of the remaining itaconic acid depending upon the composition of the solution and the analysis of electrodeposition current curve.

EXAMPLE 1.

In the same manner as in the Comparative Example, the following compounds were subjected to the same polymerization conditions as in the Comparative Example to obtain a resin solution 2a:

Tridecyl methacrylate	35.9	parts by weight
Styrene	26.3	parts by weight
2-Hydroxyethyl methacrylate	11.6	parts by weight
n-Butoxymethyl acrylamide	13.3	parts by weight
Itaconic acid	3.9	parts by weight
Azobisisobutyronitrile	2.81	parts by weight
2-Mercaptoethanol	1.07	parts by weight
Isopropyl alcohol	78.1	parts by weight

The resin solution 2a had a pKa (r) value of 9.10 and n of 1.16. To the resin solution 2a was added β-dimethylaminoethanol so that the degree of neutralization might become 45%, and to 100 parts by weight of the thus neutralized resin solution was added 30 parts by weight of hexakismethoxymethyl melamine resin, and the resulting mixture was well stirred to obtain a resin solution 2b.

With 120 parts by weight of the resin solution 2b was mixed 75 parts by weight of titanium oxide (JR—600E) and milled on a ball mill for 24 hrs. after which 240 parts by weight of the resin solution 2b was further added and milled for 24 hours. To obtain a white enamel paste 4a.

To the white enamel paste 4a were added deionized water and an OH-type anion exchange resin (Diaion SA—20A, a trademark of Mitsubishi Kasei Kogyo Kabushiki Kaisha) having a particle diameter of 50 to 200 mesh in proportions of 50 g and 6 g, respectively, per 1 kg of the paste, and the resulting mixture was mixed at 40°C. for 3 hours., after which the ion exchange resin powder was removed by filtration to obtain a white enamel paste 4b.

The white enamel paste 4b was diluted with deionized water to a solid content of 35% and a H-type cation exchange resin (Diaion WK—10, a trademark of Mitsubishi Kasei Kogyo Kabushiki Kaisha) was added thereto in a proportion of 10 g per 1 kg of the resin solution, and the resulting mixture was stirred for about 30 min. upon which the pH of the resin solution was changed from 9.24 to 8.1—8.5. The H-type cation exchange resin was removed from the resin solution by filtration to obtain a resin solution, which is designated as 5a. The coating dispersion 6a was diluted with water to a solids concentration of about 15 %, which is designated as 6b. The coating dispersion 6a was separately diluted with an aqueous coating bath to a solids concentration of about 15 %, which is designated as 6c.

White enamel paste 4b was diluted to a solids content of about 15 %, which is designated as 6d.

The coating dispersion 6a was diluted with the coating bath 6c to obtain a coating bath, which is designated as 6e.

Using the coating baths 6b, 6d and 6e as aqueous coating bath and replenishing coating composition, electrodeposition coating was effected in the same manner as in the Comparative Example to obtain results as shown in Table 4, in which the coating rate was 0.2 turnover per day.

TABLE 4

Bath: Resin solution for preparation of bath	Bath: Replenishing resin solution	Turnover	N.V. (%)	pH	K/C	Amine content* (%)
6d	6d	0	15.0	8.8	0.189	14.2
		1	14.9	9.1	0.260	18.0
		2	15.0	9.7	0.330	22.0
		3	15.1	9.9	0.410	26.0
6b	6 b	0	15.0	8.1	0.145	11.0
		1	15.1	8.15	0.200	11.2
		2	15.1	8.10	0.244	11.4
		3	15.1	8.12	0.247	12.5
6b	6e	0	15.1	8.08	0.145	11.1
		1	15.1	8.11	0.210	11.1
		2	15.1	8.12	0.233	11.2
		3	15.1	8.11	0.247	11.3

Note: N.V. and K/C are the same as above, and * corresponds to C_b in equation [D].

EXAMPLE 2.

[I] To 150 g of the white enamel paste 4b used in Example 1 was added 4.25 g of an anticorrosive pigment Organochrome (A) (made by Taito Pfizer) and these were mixed for 24 hrs., after which 300 g of white enamel paste 4b was added thereto and the resulting mixture was mixed for 24 hrs. to obtain a paste, which is designated as 7a.

Paste 7a (24 g), white enamel paste 4b (96 g) and deionized water (380 g) were mixed to obtain a coating bath, which is designated as 7b.

[II] The neutralized resin solution of 2a (α=0.45) obtained in Example 1 was mixed with the same anticorrosive pigment in the same manner as in above [I] to obtain a paste, which is designated as 7c.

The same procedure as in the production of dispersion 6a in Example 1 was repeated, except that the white enamel paste 4b was diluted with deionized water to a solids con-

tent of 15%, to obtain a coating bath 5*a*.

[III] The coating bath 7b, paste 7c, white enamel paste 4b, the coating bath 5a and the white enamel paste 2b′ were diluted with deionized water to a solids concentration of 15 % to prepare aqueous coating baths. The mechanical stability of the resulting aqueous coating baths was as shown in Table 5. In the baths, electrodeposition coating was effected at 120—250V for an electrodeposition period of 2.5 min. In the same manner as in the Comparative Example, and the resulting film was baked at 180°C for 30 min. The properties of the films obtained were as shown in Table 5.

TABLE 5

Run No.	Paste or bath used	Days after preparation of bath	Gloss (%)	Film thickness (μ)	N.V. (%)	pH	K/C	*1 Mechanical stability	*2 Corrosion resistance
1	7b	0	82.5	30	14.1	8.9	0.23	29	1.5
		7	82.3	29	15.7	8.8	0.44		
2	5a	0	–	–	–	–	–	68	1.5
		7	–	–	–	–	–		
3	2b'	0	–	–	–	–	–	81	4
		7	–	–	–	–	–		
4	4b	0	–	–	–	–	–	10	2
		7	–	–	–	–	–		
5	7c	0	82.0	30	15.0	9.12	0.25	100	1.5
		7	82.5	28	13.1	9.10	0.48		

Note: N.V. and K/C are the same as defined above

*1 Measured by means of a homogenizer which can be rotated at a high speed (500—12,000 rpm.). 100 g of a bath liquid was placed in a 100 cc beaker and agitated at 8,000 rpm. for 10 min., and the amount of precipitate was measured. The amount of precipitate of No. 5 was defined as 100, and the amounts of precipitates of Nos. 1 to 4 are shown in ratio to No. 5. The smaller the figure, the better the stability of bath.

*2 A film obtained by electrodeposition coating was baked, and then the coated panel was cross linked and treated with salt solution spray at 40°C for 150 hrs., after which the cross-cut parts were peeled off by means of Scotch tape. The width of peeling on one side is shown in mm.

Our copending applications Nos. 3148/74 Serial No. 1,381,299 and 4828/74 Serial. No. 1,381,300 describe and claim methods for preparing aqueous coating compositions which are usable in the present process.

WHAT WE CLAIM IS:—

1. A process for controlling an aqueous coating bath containing a water-soluble or dispersible paint binder, which comprises:

(a) copolymerizing (1) 5 to 80 mole percent of at least one compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-COOR_1 \qquad (E)$$

wherein R is H or CH_3 and R_1 is a straight or branched alkyl group having 1 to 18 carbon atoms or benzyl, (2) from 0.1 to 60 mole percent of a compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-CONHR_3 \qquad (F)$$

wherein R is the same as defined above, R_3 is H or a $-CHR_4OR_5$ group in which R_4 is hydrogen or an alkyl group having 1 to 8 carbon atoms and R_5 is a straight, branched or cyclic alkyl group having 1 to 8 carbon atoms and/or a compound represented by the formula,

$$CH_2=\overset{\displaystyle R}{\overset{|}{C}}-COOR_6OH \qquad (G)$$

wherein R is the same as defined above, and R_6 is a substituted or unsubstituted alkylene having 1 to 8 carbon atoms, (3) 1 to 30 mole percent of (H) an α,β-monoethylenically unsaturated carboxylic acid or its anhydride and (4) 5 to 40 mole percent of (I) at least one other vinyl monomer copolymerizable with the monomers (E) to (H), the total sum of components (E) to (I) being 100 mole percent, to prepare a paint binder, the paint binder being composed mainly of a partial neutralization salt of a polycarboxylic acid resin having a pKa(r) and an n value defined by the equation [A] and low molecular weight acids or their salts having a pKa(e) value defined by the equation [B], the main polycarboxylic acid resin having, when the paint binder is diluted with water, an average pKa(r) value defined by the formula [A] of 8.0 or more and having an n value of $0.8\leqq n\leqq 2.5$,

$$pH=pKa(r)+n\log\frac{\alpha}{1-\alpha} \qquad [A]$$

wherein pKa(r) is a constant represented by $-\log Ka(r)$ in which Ka(r) is the dissociation constant of the acid groups of the polycarboxylic acid resin in water; α is the degree of neutralization of the whole of the acid groups of the polycarboxylic resin with a neutralizing agent and has a value within the range defined by $0.15\leqq\alpha\leqq 0.80$; and n is a constant obtained experimentally by use of the equation [A] and has a value within the range defined by $0.8\leqq n\leqq 2.5$; the pKa(e) value defined by equation [B] when the low molecular weight acids or their salts in the paint binder are diluted with water being at least 0.5 smaller than the pKa(r) value of the main polycarboxylic acid resin constituting the paint binder

$$pH=pKa(e)+\log\frac{\alpha}{1-\alpha} \qquad [B]$$

wherein pKa(e) is a constant represented by $-\log Ka(e)$ in which Ka(e) is the dissociation constant of the low molecular weight acids or their salts in water; α is the degree of neutralization of the whole of the acid groups of the low molecular weight acids with a neutralizing agent; (b) adding an anion exchanger to the paint binder or its partial neutralization product alone or in admixture with a pigment and, if necessary, a small amount of water with stirring to react the low molecular weight acids or their salts with the anion exchanger and then removing the anion exchanger from the paint binder to make the content of the low molecular weight acids or their salts in the paint binder up to 5%,

(c) adding up to 60% by weight of deionized water or water which constitutes a coating bath, or water obtained by removing the paint particles from a coating bath to the paint binder obtained in above (b) and then contacting the paint binder with a cation exchanger, thereby reacting the cation exchanger with the excess neutralizing agent contained in the paint binder and then removing the cation exchanger from the paint binder,

(d) diluting the paint binder obtained in above (c) with deionized water to a given concentration to prepare an aqueous coating bath, and

(e) supplying to the aqueous coating bath the paint binder obtained in above step (c) to control the paint concentration of the aqueous coating bath to a given value in order to prevent the reduction of the paint concentration of the aqueous coating bath due to the paint being taken out of the coating bath with the progress of coating in the aqueous coating bath obtained in above (d).

2. A method according to claim 1, wherein the treatment of the paint binder in step (b) is effected by adding to the polycarboxylic acid resin or its salt an OH type anion

exchange resin having a particle size of 1,200 microns or less, and if necessary, water, and then agitating the resulting mixture.

3. A method according to claim 1, wherein the treatment of the paint binder in step (b) is effected by mixing a salt of the polycarboxylic acid resin with a pigment to form an enamel, adding to the enamel an OH type anion exchange resin having a particle size smaller than 1,200 microns, and, if necessary, water, and then stirring the resulting mixture.

4. A method according to claim 1, wherein the treatment of the paint binder in step (b) is effected by mixing a salt of the polycarboxylic acid resin with a pigment and an OH type anion exchange resin having a particle size smaller than 1,200 microns, and, if necessary, water and then grinding the resulting mixture.

5. A method according to claim 1, wherein the α,β-monoethylenically unsaturated carboxylic acid or its anhydride (H) is a monomer having the formula (Z), and/or its half alkyl ester:

$$CH_2{=}\underset{\underset{(CH_2)_mCOOH.}{|}}{C}{-}COOH \qquad (Z)$$

wherein m is 1 or 2.

6. A method according to claim 1, wherein the polycarboxylic acid resin is in the form of a mixture with an epoxy resin and/or a melamine resin in a ratio of 100/0 to 60/40.

7. A method according to claim 5, wherein the (2) component consists of 5 to 40 mole percent of the formula (F) monomer and 5 to 40 mole percent of the formula (G) monomer, the total sum of the two being 10 to 60 mole percent.

8. A method according to claim 1, wherein in step (b) 15% by weight or less of water is added to the salt of the polycarboxylic acid resin or its salt and the resulting mixture is treated with an OH type anion exchange resin.

9. A method according to claim 1, wherein the cation exchanger used in step (c) is an H type cation exchange resin.

10. A method according to claim 1, wherein the solid content of the aqueous coating bath obtained in the (d) step is 1—20% by weight.

11. A method according to claim 10, wherein the coating is an electrodeposition coating.

12. A method according to claim 4, wherein the pigment comprises mainly an inorganic pigment and anti-corrosive pigment.

13. A process for controlling an aqueous coating bath, substantially as herein described with reference to the Examples.

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